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IRON ORES - DETERMINATION OF Fe(II) BY TITRIMETRIC METHOD

STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA - 1982

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Project MRP-3.8.0.0.11
Analytical Methodology

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IRON ORES - DETERMINATION OF Fe(II) BY TITRIMETRIC METHOD STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA - 1982

by

R. Sutarno* and W.S. Bowman**

SUMMARY

The analytical data resulting from the international test conducted on the determination of Fe(II) by titrimetric method conducted by ISO/TC 102/SC2/WG 20A have been statistically evaluated. Based on these analytical results, the precision of the analytical method can be expressed in terms of the Fe(II) concentration level by the following equations:

$$r = 0.0090\ X + 0.0942$$
$$P = 0.0217\ X + 0.4555$$
$$\sigma_r = 0.0032\ X + 0.0333$$
$$\sigma_L = 0.0073\ X + 0.1596$$

where X is the Fe(II) concentration in the sample, r is the repeatability, P is the permissible tolerance, σ_r is the within-laboratory standard deviation and σ_L is the between-laboratories standard deviation all in mass %. Five samples containing Fe(II) ranging from 0.7 to 27.5% were used in this international test.

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INTRODUCTION

The analytical data were collected by the convener of ISO/TC102/SC2/WG 19 B (Technical Committee 102 - Iron Ores, Subcommittee 2 - Chemical Analysis, Working Group 19 B - Determination of vanadium by spectrophotometric method) from an international test conducted during the period 1980 - 1982[1]. Eight samples of iron ores with vanadium contents ranging from 0.005 to 0.5% were used. Twelve laboratories provided analytical data; each analyzed two bottles of sample of each ore in duplicate.

The purpose of this statistical evaluation is to provide the working group with estimates of the precision in the form of repeatability, permissible tolerance, and within - laboratory and between - laboratories standard deviations.

PRINCIPLE OF ANALYTICAL METHOD

Decomposition of the test portion is accomplished by fusion or sintering with sodium peroxide and leaching with water and sulphuric acid. Copper sulphate and potassium permanganate are added to an aliquot to oxidize vandium to the quinquevalent state; samples are then treated with BPHA and hydrochloric acid to form a complex which is extractioned into chloroform. Spectrophotometric measurement of the absorbance is made at approximately 535 nm and compared to absorbance values of calibration solution treated in the same manner.

STATISTICAL EVALUATION

The analytical data were statistically evaluated using the procedure described in ISO/TC102/SC2 N532E (factor 2.77 has been replaced by 2.83)[2] This procedure is schematically illustrated in Figure 1. The raw data are also plotted in Figures 2. The boxed points in these figures signify that these data are suspected outliers and were not used to estimate the grand means and precisions. The estimated precisions are plotted against their corresponding grand means in Figures 3. In Figure 3.1 the precisions estimated from all eight samples are plotted. In Figure 3.2 the

OBSERVATIONS

Based on the results of statistical evaluation, the following observations may be noted:

1. The within-laboratory standard deviations, σ_r, are reasonable for the the concentration level (Table 1). However, the between-laboratory standard deviations, σ_L, are rather large (Table 2). The σ_L / σ_r ratios are greater than normally acceptable for ISO standards for iron ores analysis.

2. The number of outliers is greater than expected from statistical cause (Table 2); most outliers result from lack of precision (Cochran's test). Some laboratories seem to have problems performing the analytical procedures. These laboratories reported outliers on more than one sample.

3. The functional relationship between precision and concentration level (Table 1, Figure 3), particularly the within-laboratory precision, is good.

Based on the above observations, it could be inferred that the analytical method seems to behave consistently over the concentration range. However, further standardization is still necessary to improve the between-laboratories repeatability and to solve the difficulties experienced by some laboratories.

REFERENCES

1. "Determination of Iron (II) content - titrimetric method"; ISO/TC 102/SC 2 (WG 20 A - 1); September, 1981.

2. "Procedure for statistical evaluation of analytical data resulting from international tests"; ISO/TC 102/SC 2 (WG 7-21) N 532 E; August, 1978.

Table 1.

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD

SUMMARY OF PRECISIONS FOR ALL SAMPLES

SAMPLE	MEAN(X)	REPEATABILITY	PERMISSIBLE TOLERANCE	SIGMA-R	SIGMA-L
1 (81/7)	.7781	.0940	.3538	.03322	.12281
2 (81/8)	5.9811	.1917	.7100	.06773	.24626
3 (81/9)	13.4149	.1902	.8152	.06722	.28411
4 (81/10)	22.5456	.2122	.8489	.07499	.29523
5 (81/11)	27.3174	.4122	1.0712	.14566	.36424

THE REGRESSION EQUATIONS ARE:					CORR. COEFF.
R	=	.0090 X	+	.0942	.8518
P	=	.0217 X	+	.4555	.9166
SIGMA-R	=	.0032 X	+	.0333	.8518
SIGMA-L	=	.0073 X	+	.1596	.9138

Table 2 - List of outliers - Determination of Fe(II) by titrimetric method

Sample No.	K_o	N_o	K	N	OUTLIERS			σ_L/σ_r
					Laboratory		Individual results	
					Cochran (precision)	Dixon (accuracy)		
1 (81/7)	23	92	21	83	UK 3	AU 2	AU 1	3.7
2 (81/8)	23	92	19	76	AU 1 FR 2 UK 3	UK 1	-	3.6
3 (81/9)	23	92	22	86	AU 2	-	AU 1 AU 5	4.2
4 (81/10)	23	92	18	72	AU 1 AU 2 AU 5 UK 2 UK 3	-	-	3.9
5 (81/11)	23	92	22	88	FR 2	-	-	2.5

K_o - original number of sets of laboratory results

K - number of **sets of laboratory results for one way ANOVA**

N_o - original number of results

N - number of results used for one way ANOVA

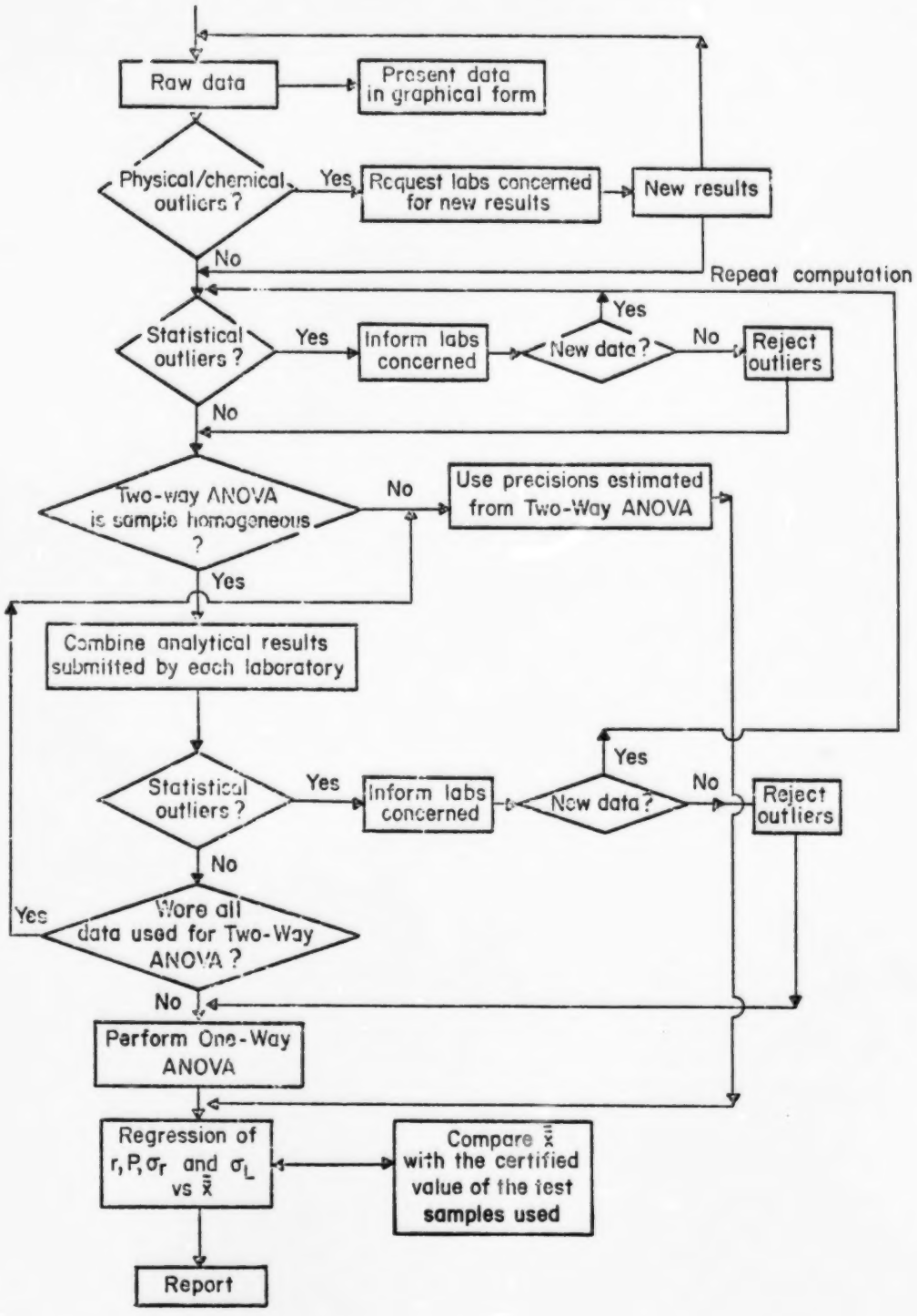

Figure 1. Flow Chart of the Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests.

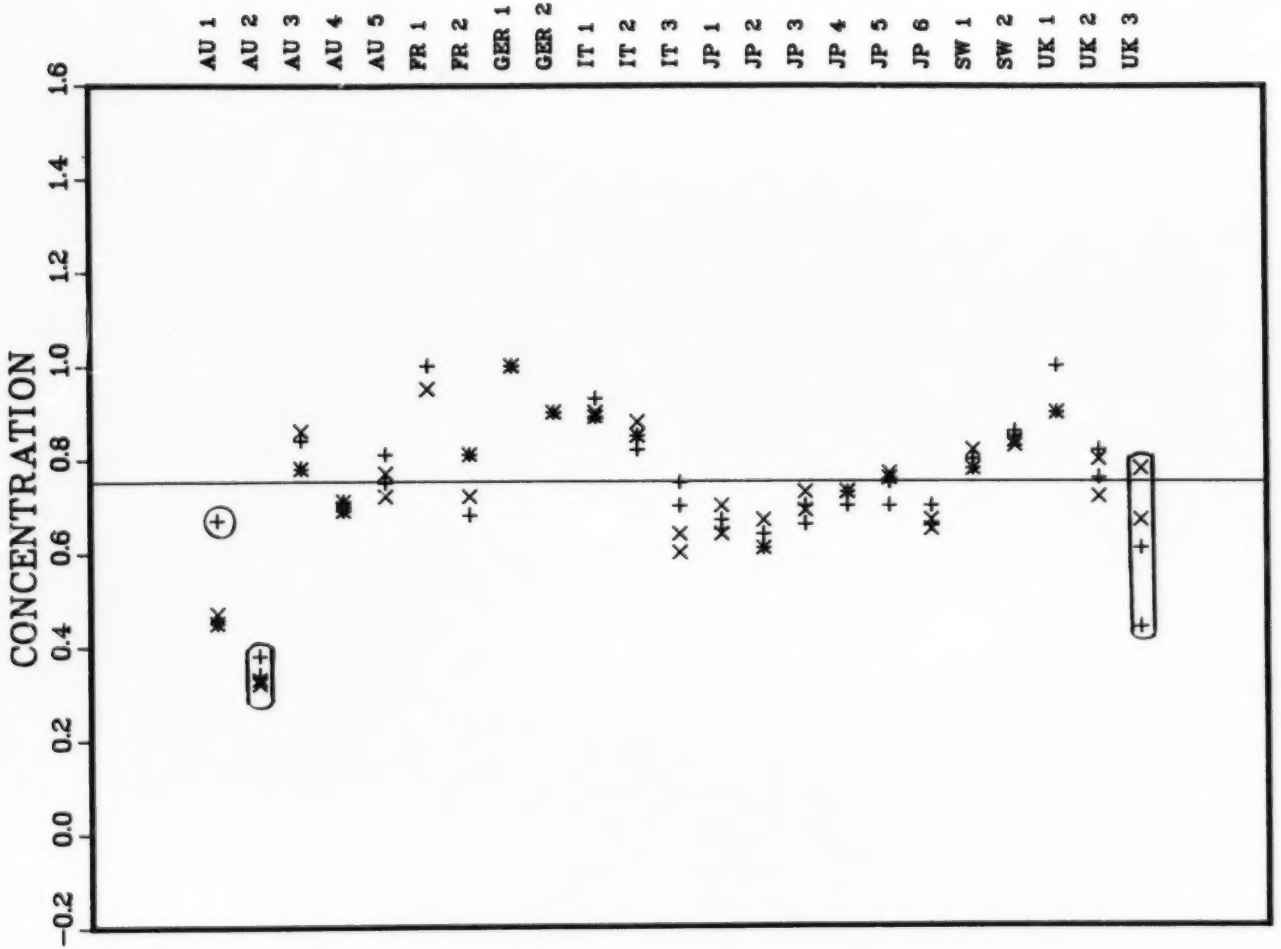

Figure 2.1 **ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD**
SAMPLE: 1(81/7)

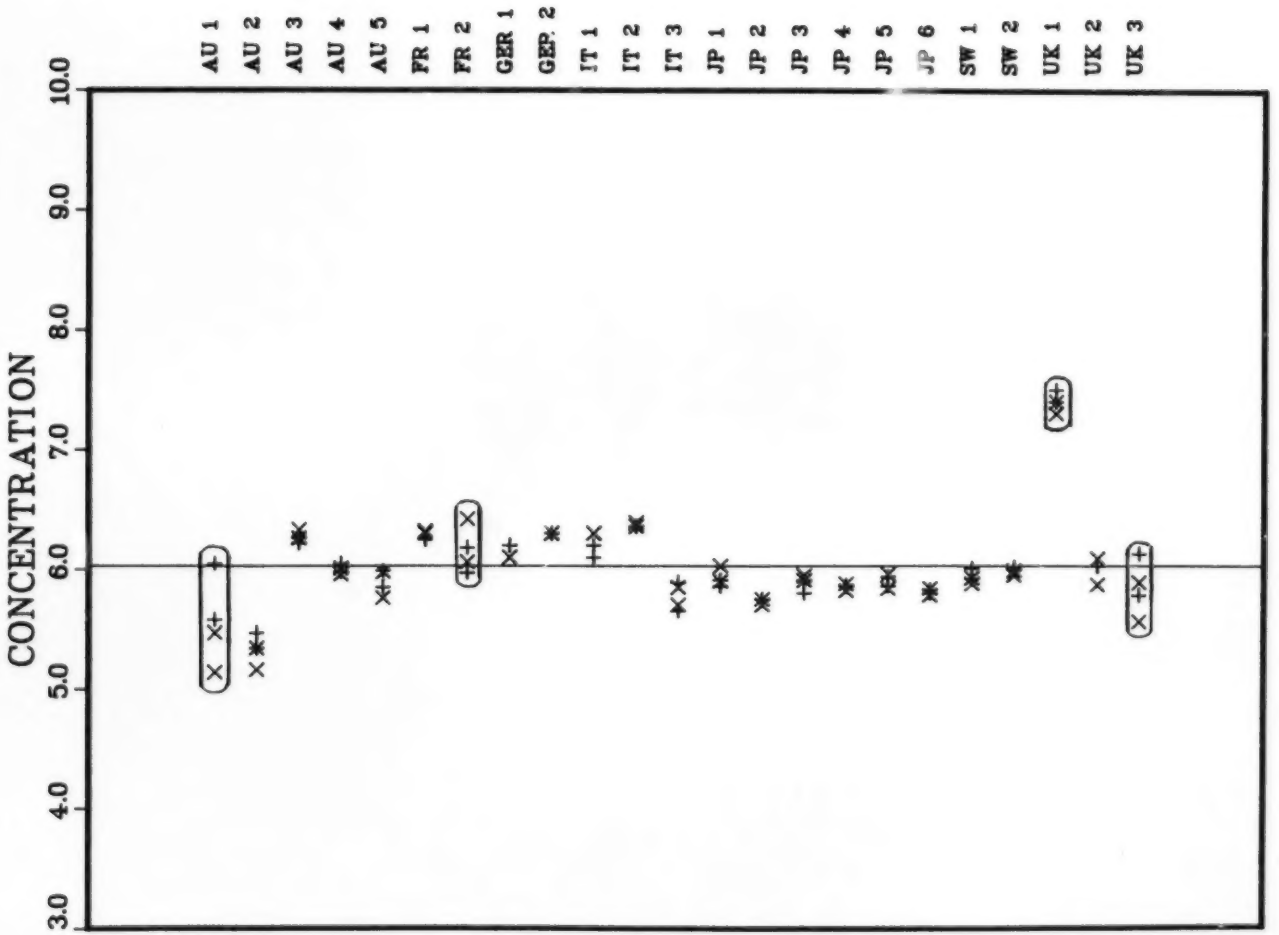

Figure 2.2 **ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD**
SAMPLE: 2(81/8)

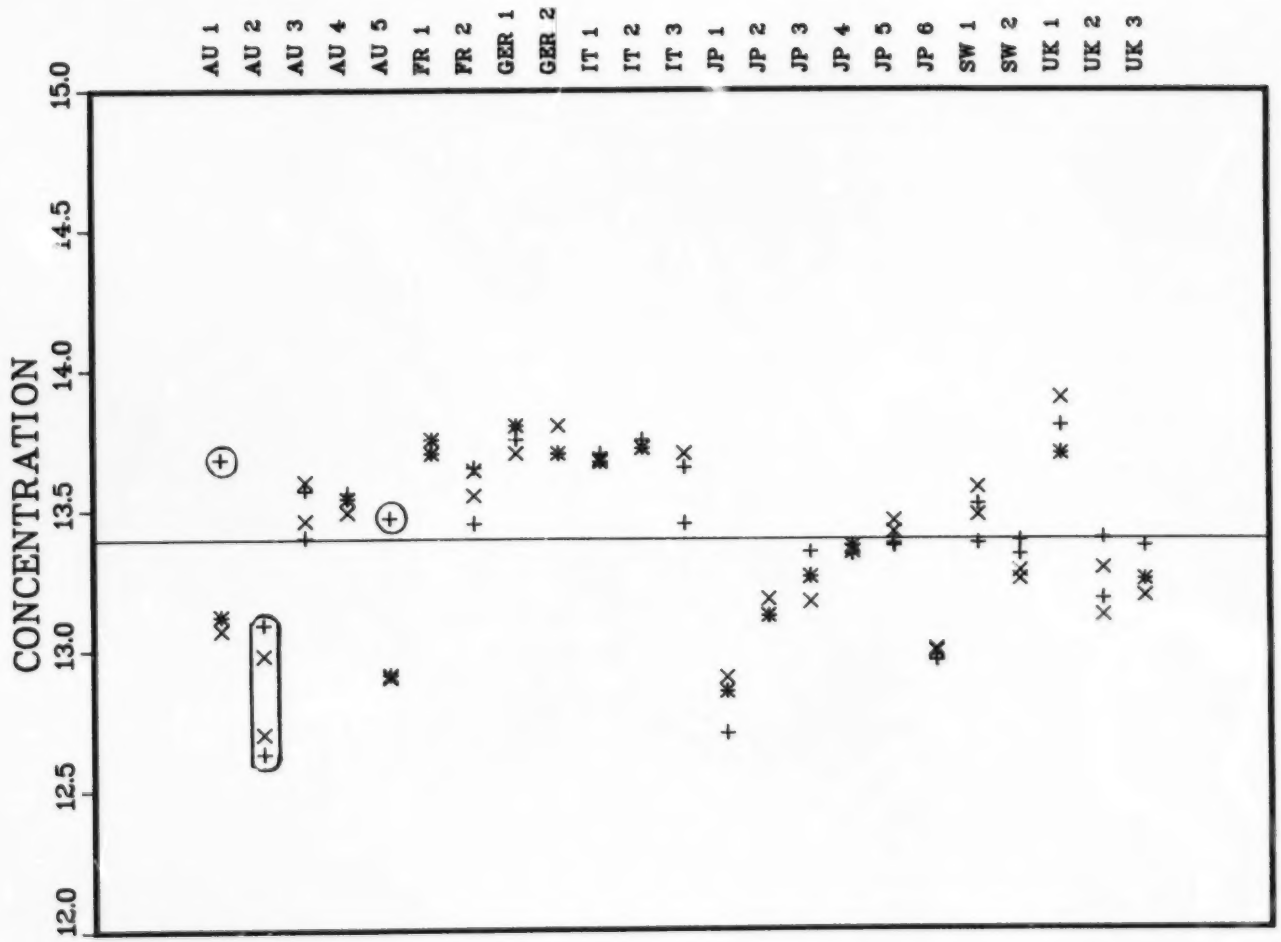

Figure 2.3 ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

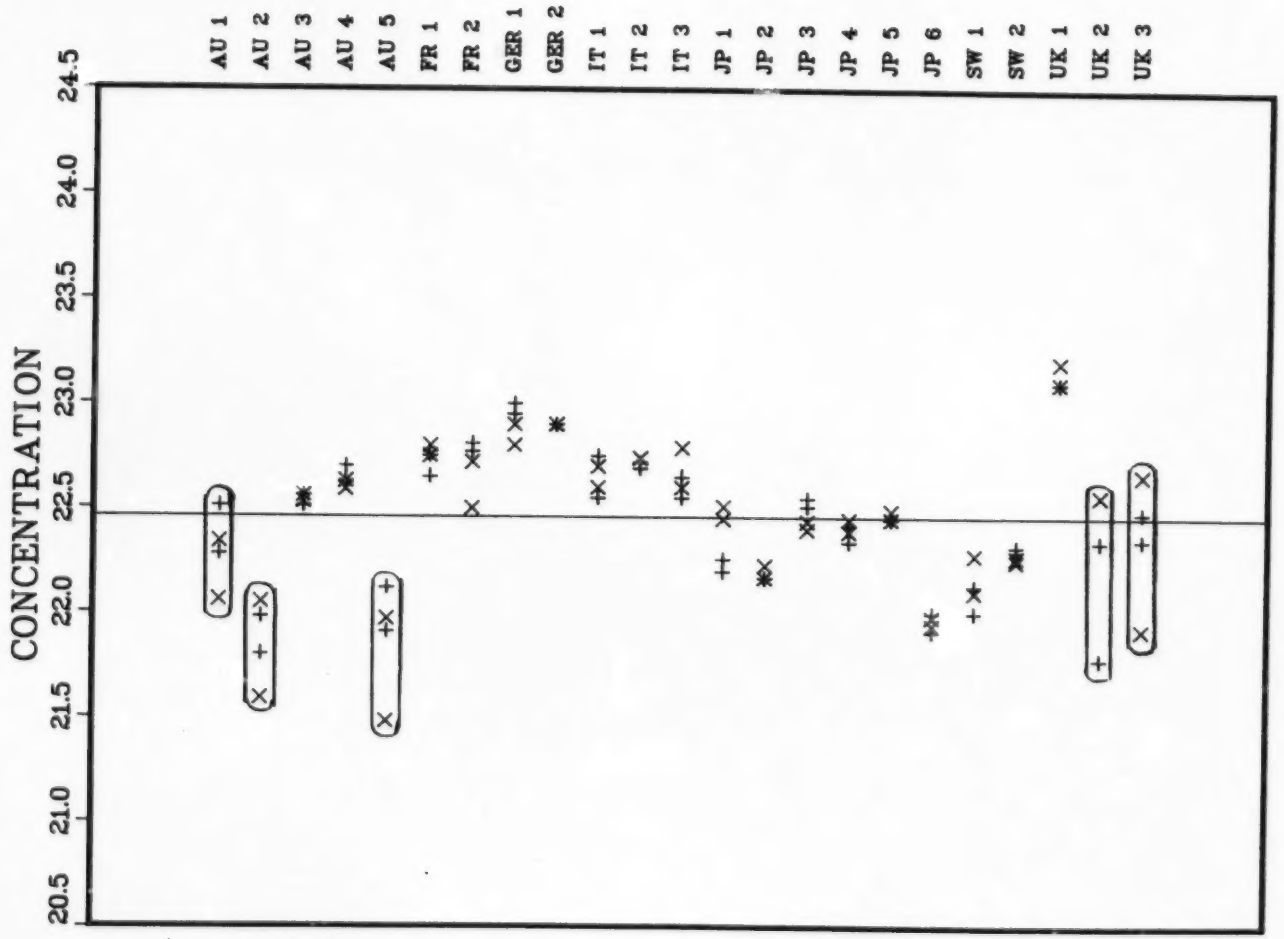

Figure 2.4 **ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD**
SAMPLE: 4(81/10)

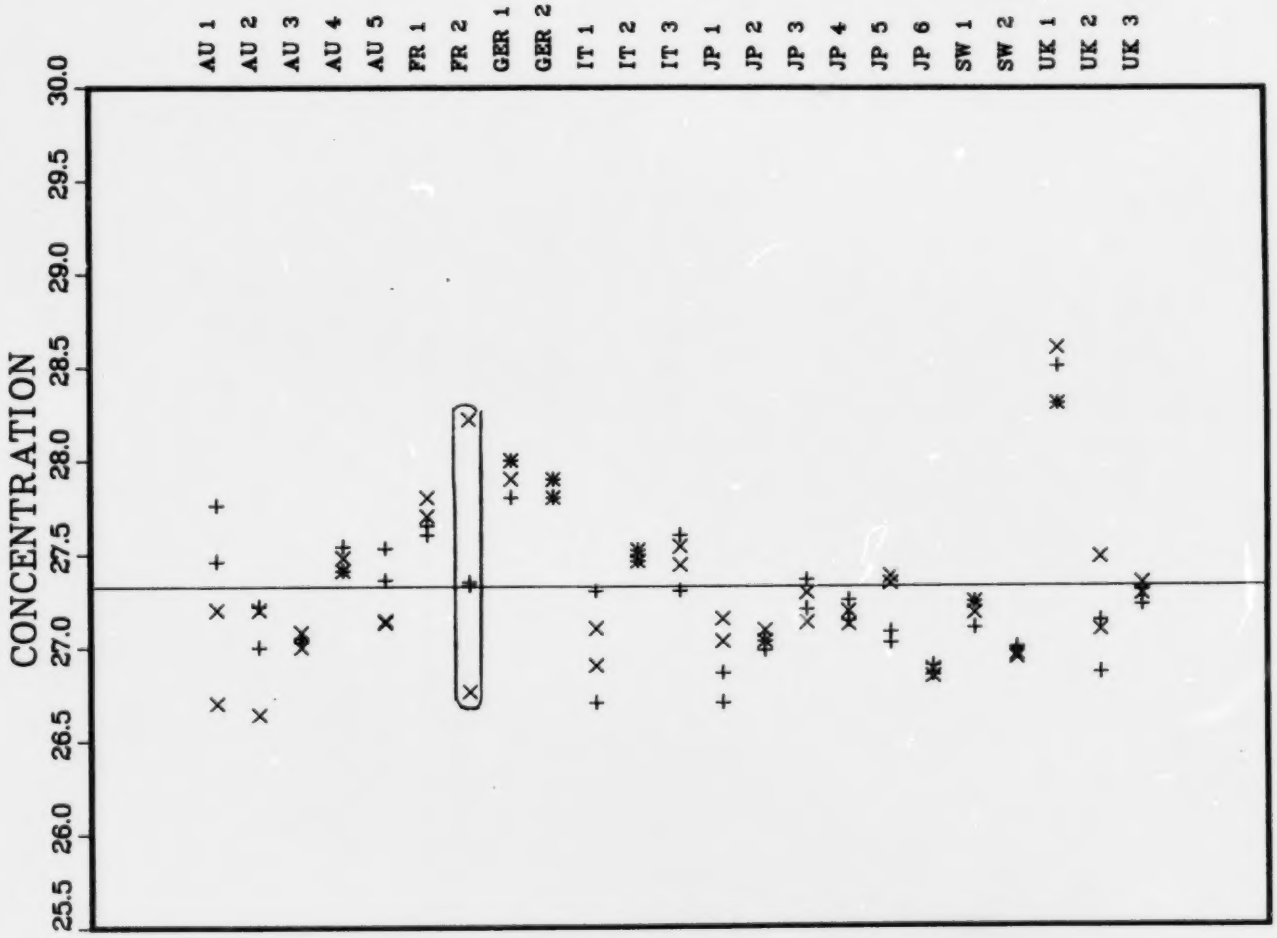

Figure 2.5 **ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD**
SAMPLE: 5(81/11)

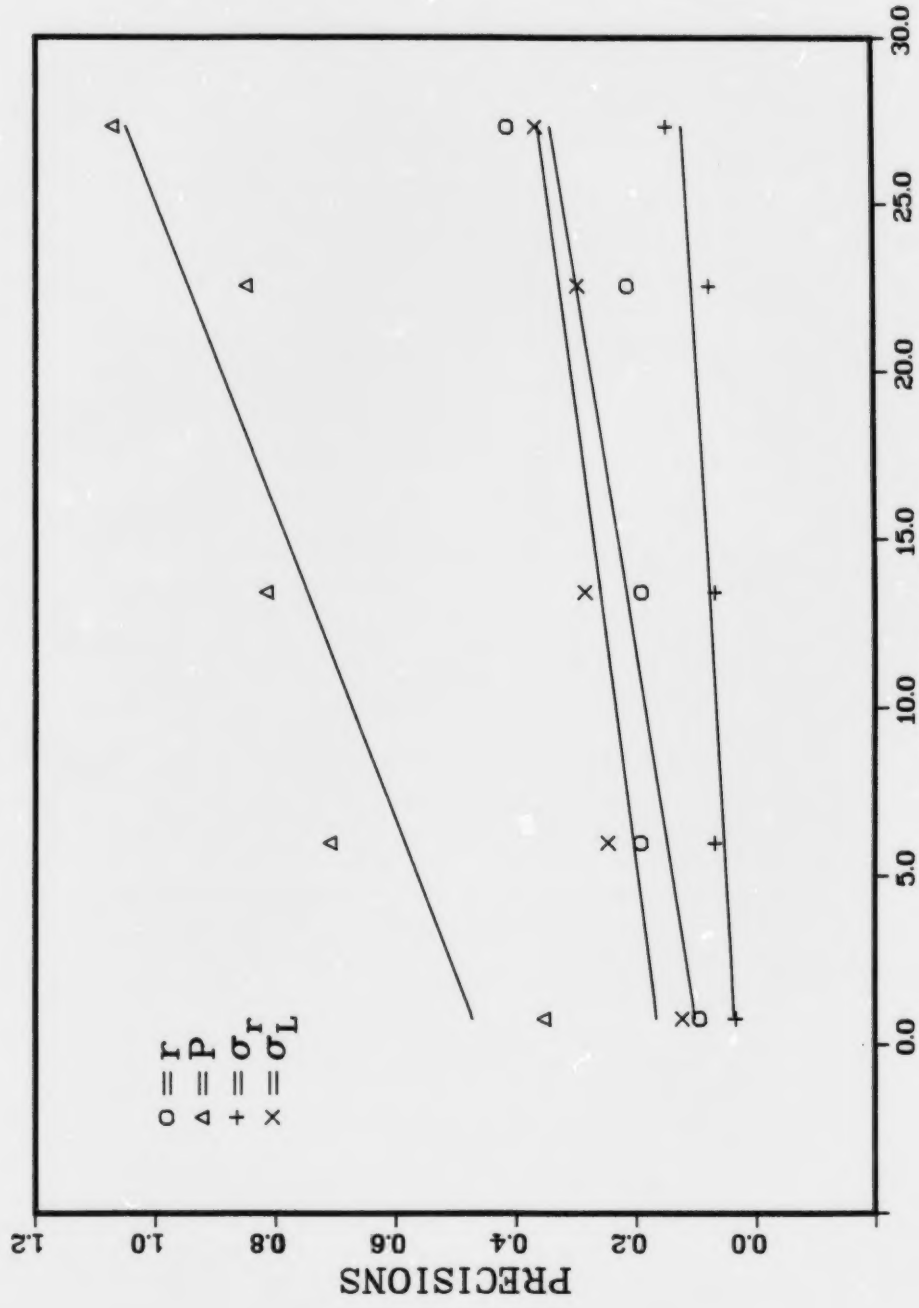

Figure 3 ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD

APPENDIX

DETAILED COMPUTATION OF THE ANALYTICAL DATA

Key to the abreviations and symbols

r = R - repeatability

P = permissible tolerances - between laboratories

σ_r = SIGMA-R - within laboratory - standard deviation

σ_L = SIGMA-L - between laboratories - standard deviation

Au = Australia

FR = France

GER = Germany

IT = Italy

JP = Japan

SW = Sweden

UK = United Kingdom

$Fe^{+?}$ = Fe(II) = Iron (II)

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
1	AU 1	1	.4500	.4700	.51000	.1147E-01
		2	.4500	.6700		
2	AU 2	1	.3300	.3200	.34250	.6917E-03
		2	.3400	.3800		
3	AU 3	1	.8600	.7800	.81500	.1700E-02
		2	.8400	.7800		
4	AU 4	1	.6900	.7100	.70000	.1333E-03
		2	.6900	.7100		
5	AU 5	1	.7700	.7200	.76250	.1425E-02
		2	.8100	.7500		
6	FR 1	1	.9500	.9500	.97500	.8333E-03
		2	1.0000	1.0000		
7	FR 2	1	.7200	.8100	.75500	.4300E-02
		2	.6800	.8100		
8	GER 1	1	1.0000	1.0000	1.00000	0.
		2	1.0000	1.0000		
9	GER 2	1	.9000	.9000	.90000	0.
		2	.9000	.9000		
10	IT 1	1	.8900	.9000	.90250	.3583E-03
		2	.8900	.9300		
11	IT 2	1	.8500	.8800	.85000	.6000E-03
		2	.8200	.8500		
12	IT 3	1	.6400	.6000	.67250	.4358E-02
		2	.7000	.7500		
13	JP 1	1	.7000	.6400	.66500	.7000E-03
		2	.6700	.6500		
14	JP 2	1	.6100	.6700	.63250	.8250E-03
		2	.6100	.6400		
15	JP 3	1	.7300	.6900	.69500	.8333E-03
		2	.7000	.6600		
16	JP 4	1	.7300	.7300	.72250	.2250E-03
		2	.7000	.7300		
17	JP 5	1	.7600	.7700	.74500	.9667E-03
		2	.7000	.7500		
18	JP 6	1	.6700	.6500	.67000	.4667E-03
		2	.6600	.7000		
19	SW 1	1	.7800	.8200	.79500	.3667E-03
		2	.7800	.8000		
20	SW 2	1	.8300	.8400	.84500	.1667E-03
		2	.8300	.8600		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
21	UK 1	1	.9000	.9000	.92500	.2500E-02
		2	.9000	1.0000		
22	UK 2	1	.8000	.7200	.77500	.1967E-02
		2	.8200	.7600		
23	UK 3	1	.7800	.6700	.62500	.2017E-01
		2	.4400	.6100		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	31.499
CHI-SQUARE(.95,35)	49.811

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

LAB- 6	ZERO WITHIN-BOTTLE VARIANCE
LAB- 8	ZERO WITHIN-BOTTLE VARIANCE
LAB- 9	ZERO WITHIN-BOTTLE VARIANCE
LAB-16	ZERO WITHIN-BOTTLE VARIANCE
LAB-21	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	17	.11879125E+01	.69877206E-01
BETWEEN BOTTLES	18	.69725000E-01	.38736111E-02
WITHIN BOTTLES	36	.84750000E-01	.23541667E-02
TOTAL	71	.13423875E+01	

F-CALC = 1.645 F-CRIT(.95;18,36) = 1.899

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC 51.873
CHI-SQUARE(.95,20) 31.416

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB-23 C-CALC = .366 C-CRIT(4,21) = .212

LAB- 1 C-CALC = .329 C-CRIT(4,20) = .220

BOTTLE- 2 REPLICATE- 2 DIXON'S TEST WITHIN LAB- 1
R10 = .909 D-CRIT(4) = .829

DIXON'S TEST FOR LABORATORY MEANS

LAB- 2 R = .485 D-CRIT(23) = .459

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 2 DIXON'S TEST FOR LABORATORY MEANS
LAB-23 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

LAB- 1 BOTTLE- 2 REPLICATE- 2 .6700

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 1(81/7)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	20	.12140499E+01	.60702495E-01
WITHIN LABS	62	.68441667E-01	.11038978E-02
TOTAL	82	.12824916E+01	

REPEATABILITY VARIANCE	.11038978E-02
REPEATABILITY STD. DEV.	.03322496
BETWEEN-LABORATORIES VARIANCE	.15081352E-01
BETWEEN-LABORATORIES STD. DEV.	.12280616
REPEATABILITY	.09402663
PERMISSIBLE TOLERANCE BETWEEN LABS	.35384396
GRAND MEAN	.77807229
VARIANCE OF THE GRAND MEAN	.73354455E-03

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
1	AU 1	1	5.1400	5.4700	5.56000	.1417E+00
		2	5.5800	6.0500		
2	AU 2	1	5.3400	5.1600	5.32750	.1623E-01
		2	5.4700	5.3400		
3	AU 3	1	6.3300	6.2600	6.26750	.2092E-02
		2	6.2600	6.2200		
4	AU 4	1	5.9600	6.0100	6.00000	.1533E-02
		2	5.9800	6.0500		
5	AU 5	1	5.7600	5.9800	5.89500	.1217E-01
		2	5.8500	5.9900		
6	FR 1	1	6.3200	6.3000	6.28000	.1267E-02
		2	6.2500	6.2500		
7	FR 2	1	6.0600	6.4200	6.15750	.3803E-01
		2	6.1800	5.9700		
8	GER 1	1	6.1000	6.1000	6.15000	.3333E-02
		2	6.2000	6.2000		
9	GER 2	1	6.3000	6.3000	6.30000	0.
		2	6.3000	6.3000		
10	IT 1	1	6.3000	6.3000	6.22500	.9167E-02
		2	6.1000	6.2000		
11	IT 2	1	6.3600	6.3900	6.36750	.2250E-03
		2	6.3600	6.3600		
12	IT 3	1	5.7000	5.8500	5.77250	.1336E-01
		2	5.8900	5.6500		
13	JP 1	1	6.0300	5.9000	5.92500	.5367E-02
		2	5.9100	5.8600		
14	JP 2	1	5.7500	5.7000	5.73750	.6250E-03
		2	5.7500	5.7500		
15	JP 3	1	5.9100	5.9500	5.89250	.4158E-02
		2	5.8000	5.9100		
16	JP 4	1	5.8800	5.8200	5.85750	.6917E-03
		2	5.8700	5.8600		
17	JP 5	1	5.9600	5.8400	5.90000	.3467E-02
		2	5.9400	5.8600		
18	JP 6	1	5.8400	5.7800	5.81250	.7583E-03
		2	5.8000	5.8300		
19	SW 1	1	5.8800	5.9300	5.93500	.2967E-02
		2	5.9200	6.0100		
20	SW 2	1	5.9500	5.9900	5.99000	.8667E-03
		2	6.0200	6.0000		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
21	UK 1	1	7.4000	7.3000	7.40000	.6667E-02
		2	7.4000	7.5000		
22	UK 2	1	5.8700	6.0900	6.00500	.8900E-02
		2	6.0300	6.0300		
23	UK 3	1	5.5600	5.8900	5.84000	.5620E-01
		2	5.7800	6.1300		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	29.579
CHI-SQUARE(.95,31)	44.991

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS

LAB-21	BOTTLE- 2	T-CALC = 4.377	T-CRIT(.00109,44) = 3.497
LAB-21	BOTTLE- 1	T-CALC = 5.296	T-CRIT(.00111,43) = 3.496

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

LAB- 6	ZERO WITHIN-BOTTLE VARIANCE
LAB- 8	ZERO WITHIN-BOTTLE VARIANCE
LAB- 9	ZERO WITHIN-BOTTLE VARIANCE
LAB-10	ZERO WITHIN-BOTTLE VARIANCE
LAB-11	ZERO WITHIN-BOTTLE VARIANCE
LAB-14	ZERO WITHIN-BOTTLE VARIANCE
LAB-21	DOORNBOS' TEST FOR BOTTLE MEANS
LAB-22	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	14	.27402600E+01	.19573286E+00
BETWEEN BOTTLES	15	.38817500E+00	.25878333E-01
WITHIN BOTTLES	30	.51045000E+00	.17015000E-01
TOTAL	59	.36388850E+01	

F-CALC = 1.521 F-CRIT(.95;15,30) = 2.015

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	73.834
CHI-SQUARE(.95,21)	32.678

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB- 1	C-CALC =	.430	C-CRIT(4,22) =	.204
LAB-23	C-CALC =	.299	C-CRIT(4,21) =	.212
LAB- 7	C-CALC =	.288	C-CRIT(4,20) =	.220

DIXON'S TEST FOR LABORATORY MEANS

LAB-21	R =	.662	D-CRIT(23) =	.459

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 1	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB- 7	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB-21	DIXON'S TEST FOR LABORATORY MEANS
LAB-23	COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 2(81/8)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	18	.44490158E+01	.24716754E+00
WITHIN LABS	57	.26150000E+00	.45877193E-02
TOTAL	75	.47105158E+01	

REPEATABILITY VARIANCE	.45877193E-02
REPEATABILITY STD. DEV.	.06773270
BETWEEN-LABORATORIES VARIANCE	.60644956E-01
BETWEEN-LABORATORIES STD. DEV.	.24626197
REPEATABILITY	.19168355
PERMISSIBLE TOLERANCE BETWEEN LABS	.70997935
GRAND MEAN	5.98105263
VARIANCE OF THE GRAND MEAN	.32522045E-02

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
1	AU 1	1	13.0700	13.1200	13.24750	.8369E-01
		2	13.1200	13.6800		
2	AU 2	1	12.7000	12.9800	12.85000	.4847E-01
		2	12.6300	13.0900		
3	AU 3	1	13.6000	13.4600	13.50750	.8758E-02
		2	13.5700	13.4000		
4	AU 4	1	13.5400	13.4900	13.53250	.8917E-03
		2	13.5600	13.5400		
5	AU 5	1	12.9000	12.9100	13.04750	.7936E-01
		2	13.4700	12.9100		
6	FR 1	1	13.7000	13.7500	13.72500	.8333E-03
		2	13.7500	13.7000		
7	FR 2	1	13.5500	13.6400	13.57250	.8692E-02
		2	13.6500	13.4500		
8	GER 1	1	13.8000	13.7000	13.76250	.2292E-02
		2	13.8000	13.7500		
9	GER 2	1	13.7000	13.8000	13.72500	.2500E-02
		2	13.7000	13.7000		
10	IT 1	1	13.6700	13.6800	13.68000	.2000E-03
		2	13.6700	13.7000		
11	IT 2	1	13.7200	13.7200	13.72750	.2250E-03
		2	13.7200	13.7500		
12	IT 3	1	13.7000	13.7000	13.62500	.1417E-01
		2	13.4500	13.6500		
13	JP 1	1	12.9000	12.8500	12.82500	.7500E-02
		2	12.7000	12.8500		
14	JP 2	1	13.1800	13.1200	13.13500	.9000E-03
		2	13.1200	13.1200		
15	JP 3	1	13.1700	13.2600	13.26000	.5400E-02
		2	13.3500	13.2600		
16	JP 4	1	13.3500	13.3700	13.35750	.2250E-03
		2	13.3400	13.3700		
17	JP 5	1	13.4600	13.4200	13.40750	.1692E-02
		2	13.3800	13.3700		
18	JP 6	1	13.0000	12.9900	12.97750	.4250E-03
		2	12.9600	12.9600		
19	SW 1	1	13.5800	13.4800	13.49000	.7067E-02
		2	13.5200	13.3800		
20	SW 2	1	13.2500	13.2800	13.31500	.3900E-02
		2	13.3900	13.3400		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
21	UK 1	1	13.7000	13.9000	13.77500	.9167E-02
		2	13.8000	13.7000		
22	UK 2	1	13.2900	13.1200	13.24750	.1529E-01
		2	13.4000	13.1800		
23	UK 3	1	13.2500	13.1900	13.26500	.5700E-02
		2	13.2500	13.3700		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	48.250
CHI-SQUARE(.95,35)	49.811

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

LAB- 9	ZERO WITHIN-BOTTLE VARIANCE
LAB-11	ZERO WITHIN-BOTTLE VARIANCE
LAB-12	ZERO WITHIN-BOTTLE VARIANCE
LAB-14	ZERO WITHIN-BOTTLE VARIANCE
LAB-18	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	17	.54707569E+01	.32180923E+00
BETWEEN BOTTLES	18	.23722500E+00	.13179167E-01
WITHIN BOTTLES	36	.63015000E+00	.17504167E-01
TOTAL	71	.63381319E+01	

F-CALC = .753 F-CRIT(.95;18,36) = 1.899

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	80.219
CHI-SQUARE(.95,22)	33.933

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB- 1 C-CALC = .272 C-CRIT(4,23) = .197

BOTTLE- 2 REPLICATE- 2 DIXON'S TEST WITHIN LAB- 1
R10 = .918 D-CRIT(4) = .829

LAB- 5 C-CALC = .354 C-CRIT(4,23) = .197

BOTTLE- 2 REPLICATE- 1 DIXON'S TEST WITHIN LAB- 5
R10 = .982 D-CRIT(4) = .829

LAB- 2 C-CALC = .334 C-CRIT(4,23) = .197

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 2 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

LAB- 1	BOTTLE- 2	REPLICATE- 2	13.6800
LAB- 5	BOTTLE- 2	REPLICATE- 1	13.4700

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 3(81/9)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	21	.67193405E+01	.31996860E+00
WITHIN LABS	64	.28920833E+00	.45188802E-02
TOTAL	85	.70085488E+01	

REPEATABILITY VARIANCE	.45188802E-02
REPEATABILITY STD. DEV.	.06722262
BETWEEN-LABORATORIES VARIANCE	.80717227E-01
BETWEEN-LABORATORIES STD. DEV.	.28410777
REPEATABILITY	.19024001
PERMISSIBLE TOLERANCE BETWEEN LABS	.81520048
GRAND MEAN	13.41488372
VARIANCE OF THE GRAND MEAN	.37413529E-02

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
1	AU 1	1	22.0600	22.3400	22.29750	.3456E-01
		2	22.5100	22.2800		
2	AU 2	1	21.5900	22.0500	21.85500	.4230E-01
		2	21.8000	21.9800		
3	AU 3	1	22.5600	22.5300	22.54000	.6000E-03
		2	22.5100	22.5600		
4	AU 4	1	22.6300	22.5900	22.63750	.2092E-02
		2	22.7000	22.6300		
5	AU 5	1	21.9700	21.4800	21.87000	.7540E-01
		2	21.9100	22.1200		
6	FR 1	1	22.7500	22.8000	22.73750	.3958E-02
		2	22.7500	22.6500		
7	FR 2	1	22.5000	22.7200	22.70000	.1913E-01
		2	22.7700	22.8100		
8	GER 1	1	22.8000	22.9000	22.91250	.7292E-02
		2	23.0000	22.9500		
9	GER 2	1	22.9000	22.9000	22.90000	0.
		2	22.9000	22.9000		
10	IT 1	1	22.7000	22.6000	22.65000	.8333E-02
		2	22.7500	22.5500		
11	IT 2	1	22.7400	22.7400	22.72250	.5583E-03
		2	22.6900	22.7200		
12	IT 3	1	22.6000	22.7900	22.64750	.1069E-01
		2	22.6500	22.5500		
13	JP 1	1	22.4500	22.5100	22.35500	.2203E-01
		2	22.2000	22.2600		
14	JP 2	1	22.1700	22.2300	22.18500	.9000E-03
		2	22.1700	22.1700		
15	JP 3	1	22.4000	22.4400	22.47500	.4567E-02
		2	22.5100	22.5500		
16	JP 4	1	22.3900	22.4500	22.40000	.2200E-02
		2	22.3400	22.4200		
17	JP 5	1	22.4500	22.4900	22.46250	.3583E-03
		2	22.4600	22.4500		
18	JP 6	1	21.9800	21.9400	21.95750	.1625E-02
		2	22.0000	21.9100		
19	SW 1	1	22.1000	22.2800	22.12750	.1343E-01
		2	22.0000	22.1300		
20	SW 2	1	22.2700	22.2500	22.28500	.9667E-03
		2	22.3000	22.3200		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
21	UK 1	1	23.2000	23.1000	23.12500	.2500E-02
		2	23.1000	23.1000		
22	UK 2	1	22.5600	22.5600	22.31000	.1356E+00
		2	22.3400	21.7800		
23	UK 3	1	22.6600	21.9200	22.35250	.9929E-01
		2	22.3500	22.4800		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	45.443
CHI-SQUARE(.95,35)	49.811

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

LAB- 9	ZERO WITHIN-BOTTLE VARIANCE
LAB-11	ZERO WITHIN-BOTTLE VARIANCE
LAB-14	ZERO WITHIN-BOTTLE VARIANCE
LAB-21	ZERO WITHIN-BOTTLE VARIANCE
LAB-22	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	17	.62065569E+01	.36509159E+00
BETWEEN BOTTLES	18	.30302500E+00	.16834722E-01
WITHIN BOTTLES	36	.74345000E+00	.20651389E-01
TOTAL	71	.72530319E+01	

F-CALC = .815 F-CRIT(.95;18,36) = 1.899

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	76.339
CHI-SQUARE(.95,21)	32.678

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB-22	C-CALC =	.278	C-CRIT(4,22) =	.204
LAB-23	C-CALC =	.281	C-CRIT(4,21) =	.212
LAB- 5	C-CALC =	.297	C-CRIT(4,20) =	.220
LAB- 2	C-CALC =	.238	C-CRIT(4,19) =	.229
LAB- 1	C-CALC =	.254	C-CRIT(4,18) =	.239

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 1	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB- 2	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB- 5	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB-22	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB-23	COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 4(81/10)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	17	.60226778E+01	.35427516E+00
WITHIN LABS	54	.30370000E+00	.56240741E-02
TOTAL	71	.63263778E+01	

REPEATABILITY VARIANCE	.56240741E-02
REPEATABILITY STD. DEV.	.07499383
BETWEEN-LABORATORIES VARIANCE	.87162772E-01
BETWEEN-LABORATORIES STD. DEV.	.29523342
REPEATABILITY	.21223253
PERMISSIBLE TOLERANCE BETWEEN LABS	.84888118
GRAND MEAN	22.54555556
VARIANCE OF THE GRAND MEAN	.49204884E-02

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 5(81/11)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
1	AU 1	1	27.2000	26.7000	27.28000	.2019E+00
		2	27.7600	27.4600		
2	AU 2	1	26.6400	27.2000	27.01500	.7237E-01
		2	27.0000	27.2200		
3	AU 3	1	27.0000	27.0800	27.04000	.1133E-02
		2	27.0500	27.0300		
4	AU 4	1	27.4800	27.4100	27.46000	.3933E-02
		2	27.5400	27.4100		
5	AU 5	1	27.1300	27.1400	27.29000	.3687E-01
		2	27.3600	27.5300		
6	FR 1	1	27.8000	27.7000	27.68750	.7292E-02
		2	27.6000	27.6500		
7	FR 2	1	28.2200	26.7600	27.41500	.3628E+00
		2	27.3500	27.3300		
8	GER 1	1	28.0000	27.9000	27.92500	.9167E-02
		2	27.8000	28.0000		
9	GER 2	1	27.8000	27.9000	27.85000	.3333E-02
		2	27.8000	27.9000		
10	IT 1	1	26.9000	27.1000	27.00000	.6667E-01
		2	26.7000	27.3000		
11	IT 2	1	27.5200	27.4600	27.49000	.1200E-02
		2	27.5200	27.4600		
12	IT 3	1	27.4400	27.5400	27.47000	.1720E-01
		2	27.3000	27.6000		
13	JP 1	1	27.1500	27.0300	26.93500	.3870E-01
		2	26.7000	26.8600		
14	JP 2	1	27.0900	27.0300	27.03250	.2025E-02
		2	27.0300	26.9800		
15	JP 3	1	27.1300	27.2900	27.24500	.1017E-01
		2	27.2000	27.3600		
16	JP 4	1	27.1900	27.1200	27.17500	.3367E-02
		2	27.1400	27.2500		
17	JP 5	1	27.3800	27.3400	27.20500	.3290E-01
		2	27.0800	27.0200		
18	JP 6	1	26.8800	26.8400	26.86750	.7583E-03
		2	26.9000	26.8500		
19	SW 1	1	27.2400	27.1800	27.19000	.4400E-02
		2	27.2400	27.1000		
20	SW 2	1	26.9400	26.9600	26.97250	.7583E-03
		2	27.0000	26.9900		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 5(81/11)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS		LAB MEAN	LAB VARIANCE
21	UK 1	1	28.6000	28.3000	28.42500	.2250E-01
		2	28.3000	28.5000		
22	UK 2	1	27.4800	27.0900	27.14250	.6549E-01
		2	27.1400	26.8600		
23	UK 3	1	27.3400	27.2800	27.28500	.2500E-02
		2	27.3000	27.2200		

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 5(81/11)

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	71.810
CHI-SQUARE(.95,45)	61.652

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR BOTTLE VARIANCE

LAB- 7 BOTTLE- 1 C-CALC = .533 C-CRIT(2,46) = .213

DOORNBOS' TEST FOR BOTTLE MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

LAB- 7 COCHRAN'S TEST FOR BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 20A FE(II) TITRIMETRIC METHOD
SAMPLE: 5(81/11)

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	21	.11984324E+02	.57068209E+00
BETWEEN BOTTLES	22	.88022500E+00	.40010227E-01
WITHIN BOTTLES	44	.93355000E+00	.21217045E-01
TOTAL	87	.13798099E+02	

F-CALC = 1.886 F-CRIT(.95;22,44) = 1.789

BETWEEN-BOTTLE VARIANCE IS SIGNIFICANT
TEST SAMPLE IS PRESUMED TO BE INHOMOGENEOUS

ONE-WAY ANOVA CAN NOT BE PERFORMED
PRECISION ESTIMATES FROM TWO-WAY ANOVA

REPEATABILITY VARIANCE	.21217045E-01
REPEATABILITY STD. DEV.	.14566072
BETWEEN-LABORATORIES VARIANCE	.13266797E+00
BETWEEN-LABORATORIES STD. DEV.	.36423614
REPEATABILITY	.41221984
PERMISSIBLE TOLERANCE BETWEEN LABS	1.07120823
GRAND MEAN	27.31738636
VARIANCE OF THE GRAND MEAN	.64850237E-02